

Thermodynamic Interactions and Phase Separation in a Polyolefin Blend

An Experiment Using the NG3 SANS Instrument at
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Abstract

Small-angle neutron scattering (SANS) will be used to investigate the thermodynamics of phase separation in the polyolefin blend polyethylbutylene/polymethylbutylene (PEB/PMB). The PMB polymer is deuterated for increased neutron contrast. SANS data taken at various temperatures show an intensity increase as the phase separation temperature is approached. This experiment illustrates the use of a scattering method to map out the phase separation diagram (spinodal line). The Random Phase Approximation (RPA) model will be used to fit the SANS data and a Flory-Huggins interaction parameter will be obtained. All aspects of the experiment will be discussed including sample characteristics, SANS data acquisition, data reduction and data analysis. This will be done in a hands-on format.

Introduction:

Small-Angle Neutron Scattering (SANS) is a well-established characterization method for microstructure investigations in various materials including polymers. SANS has had a major impact on the understanding of polymer conformations, morphology, rheology, and thermodynamics.

The SANS technique has matured over the years to a sophisticated tool in polymer research. Close to half of the SANS users at NIST study polymers. These users consist of hard-core professionals that are heavily invested in the use of SANS as well as occasional users that consider SANS as one of many tools at their disposal.

A hands-on experiment on a polymer blend is described here along with the SANS instrument components. Data acquisition, reduction and analysis will be carried out in a few hours time with interactive involvement of the small group of participants. The purpose is to give to junior researchers interested in polymer science a chance to perform a complete SANS experiment from a typical polymer system.

Polyolefin Blends:

Polyolefins are a wide class of polymeric materials that find uses in many aspects of our daily lives. These are polymers containing C=C double bonds either in an aromatic ring or in the aliphatic chain. These double bonds can be saturated (i.e., broken) through the hydrogenation process. Gentle interactions among polyolefin blend mixtures make them ideal "mean field" system to investigate phase separation thermodynamics. The mixed one-phase region is easily accessible for a wide range of temperatures and compositions.

Polyolefin blends are characterized by an Upper Critical Spinodal Temperature (UCST); i.e., they phase separate upon cooling down (as shown in Figure 1). Phase separation occurs either by spinodal decomposition (sinusoidal composition fluctuations) or by nucleation and growth (phase coarsening around nucleating centers). These two regions of phase separation are mapped out in Figure 1. The SANS method is used here to map out the spinodal temperature for a polyolefin blend mixture.

Theoretical Background: The Random Phase Approximation Model:

The SANS intensity increases close to the phase separation line due to enhanced composition fluctuations. Polymer thermodynamics are described by the Gibbs free energy which consists of two main contributions: one entropic part (combinatorial mixing of the monomers) and an enthalpic part (interactions between monomers).

The Flory-Huggins equation for polymer blends gives a simple expression for the Gibbs free energy:

$$G/k_B T = (\phi_1/N_1 V_1) \ln(\phi_1) + (\phi_2/N_2 V_2) \ln(\phi_2) + \chi_{12}(T) \phi_1 \phi_2 / V_0 \quad \text{Eq. 1}$$

Where N_1 , ϕ_1 and V_1 are the degree of polymerization (i.e., number of monomers per chain), volume fraction and specific volume for monomer 1 (say hPEB) and N_2 , ϕ_2 and V_2 the equivalent quantities for monomer 2 (dPMB). χ_{12} is the usual Flory-Huggins interaction parameter and V_0 is a “reference” volume.

The SANS scattering intensity is related to the second derivative of the Gibbs free energy with respect to composition. The scattering function in the forward direction ($Q=0$) is given by:

$$S^{-1}(Q=0) = (1/k_B T) \delta^2 G / \delta \phi_1^2 = (1/N_1 \phi_1 V_1) + (1/N_2 \phi_2 V_2) - 2 \chi_{12}(T) / V_0 \quad \text{Eq. 2}$$

Phase separation thermodynamics are buried in the temperature-dependent Flory-Huggins χ_{12} . For instance, the spinodal temperature is obtained from the intercept in the plot $1/S(Q=0)$ vs $1/T$ (in degrees K); i.e., scattering “blows up” at the spinodal temperature.

The Random Phase Approximation (RPA) model [1] is a mean field theory to describe polymer mixtures in the homogeneous phase region. It is a generalization of Eq. 2 to finite momentum transfer Q .

$$S^{-1}(Q) = [1/N_1 \phi_1 V_1 P_1(Q)] + [1/N_2 \phi_2 V_2 P_2(Q)] - 2 \chi_{12}(T) / V_0 \quad \text{Eq. 3}$$

Where $P_1(Q)$ is the so-called Debye function for Gaussian random polymer coils. $P_1(Q) = 2 (e^{-X} - 1 + X) / X^2$ and $X = Q^2 R_{g1}^2$ where R_{g1} is the radius of gyration for component 1. The radius of gyration can be expressed in terms of the statistical

segment length l_1 (think monomer size) as $R_{g1}^2 = nl_1^2/6$. Precisely, the statistical segment length is the length for which the polymer chain follows a random walk.

The SANS scattering intensity in terms of an absolute macroscopic cross section (units of cm^{-1}) is given by:

$$d\Sigma(Q)/d\Omega = (b_1/V_1 - b_2/V_2)^2 S(Q) \quad \text{Eq. 4}$$

where b_1/V_1 is the scattering length density for monomer 1 and the term $(b_1/V_1 - b_2/V_2)^2$ is the contrast factor. This scattering intensity is also referred to as $I(Q)$.

hPEB/dPMB Polyolefin Blends:

The polyolefin blend system used for this experiment is polyethylbutylene/polymethylbutylene (hPEB/dPMB). The PMB polymer is deuterated for enhanced neutron contrast. The chemical formula for hPEB is $[-\text{CH}_2-\text{CH}(\text{C}_2\text{H}_5)-\text{CH}_2-\text{CH}_2]-$ and for dPMB is $[-\text{CHD}-\text{CD}(\text{CH}_3)-\text{CD}_2-\text{CHD}]-$.

Scattering from an hPEB/dPMB polymer blend of molecular weight ($M_w=200\text{K}/200\text{K}$) and composition of $\phi_{\text{hPEB}}=0.25$ and $\phi_{\text{dPMB}}=0.75$ is presented here [2,3]. The scattering intensity at various temperatures is shown in Figure 2. Scattering increases for decreasing temperature, due to the approach to the phase transition (spinodal) line. The Zimm plot ($I^{-1}(Q)$ vs Q^2) yields an extrapolated value of the forward scattering $I(Q=0)$. A plot of $I^{-1}(Q=0)$ vs T^{-1} (T is in K) yields the spinodal temperature from the intercept; i.e., when $I(Q=0)$ diverges or $I^{-1}(Q=0)$ is equal to zero. Figure 3. Shows an estimated spinodal temperature of 21°C for this sample.

In order to keep a sense of discovery to this experiment, another hPEB/dPMB polyolefin blend of different molecular weight and composition will be measured instead. This sample has a $M_w=(44,100/88,400)$ and composition of $\phi_{\text{hPEB}}=0.57$ and $\phi_{\text{dPMB}}=0.43$. The stoichiometry of this sample is C_6H_{12} for hPEB and close to $\text{C}_5\text{H}_{4.5}\text{D}_{5.5}$ for dPMB.

The various parameters for the sample to be measured are:

Degree of Polymerization:	$N_1=525$	$N_2=1105$
Volume Fractions:	$\phi_1=0.57$	$\phi_2=0.43$
Specific Volumes:	$V_1=97.5 \text{ cm}^3/\text{mole}$	$V_2=81.9 \text{ cm}^3/\text{mole}$
Scattering Lengths:	$b_1=-4.99 \times 10^{-13} \text{ cm}$	$b_2=53.3 \times 10^{-13} \text{ cm}$
Segment Lengths:	$l_1=6 \text{ \AA}$	$l_2=6 \text{ \AA}$
Interaction Parameter:	$\chi_{12} = 0.011/T - 2.0 \times 10^{-5}$	T in deg K.

The segment lengths and the interaction parameter were obtained from previous measurements. The specific volumes were obtained as the ratios of the monomer molecular weight to the its density. Note that the scattering length for hPEB is negative whereas the one for dPMB is positive.

These parameters are entered into the RPA formula to obtain predictions for the SANS intensity for the sample to be measured (shown in Figure 4).

Objectives of the SANS Experiment:

The objectives of this experiment are to measure the spinodal phase separation temperature and to obtain the Flory-Huggins interaction parameter. The spinodal temperature is obtained from the intercept of the linear behavior $I^{-1}(Q=0)$ vs T^{-1} where $I(Q=0)$ is the scattering intensity in the forward direction; i.e., at $Q=0$ and T is the absolute sample temperature (in degrees Kelvin). The Flory-Huggins interaction parameter will be obtained by performing nonlinear least-squares fits to the reduced SANS data using IGOR.

Hands-on Experiment/Things to Do:

The data acquisition part of the experiment consists in measuring the hPEB/dPMB sample at 6 temperatures (10°C, 20°C, 30°C, 40°C, 50°C and 60°C) as well as the overhead runs. These runs are empty cell, blocked beam, transmission runs from the sample at every temperature and from the empty cell and measurement of the empty beam transmission for scaling of the data to an absolute cross section.

The IGOR program will be run to reduce the SANS data and produce macroscopic cross sections for each temperature. Reduced data will be plotted in a Zimm Plot form $I^{-1}(Q)$ vs Q^2 and extrapolated to obtain $I(Q=0)$. The intercept of the plot of $I^{-1}(Q=0)$ vs T^{-1} (K) yields an estimate of the spinodal temperature T_s^{-1} (this could be done using a spreadsheet program).

An IGOR Macro contains the RPA formalism, which can be run using the parameters for our hPEB/dPMB sample. Nonlinear least squares fitting to the RPA functional form will produce the statistical segment lengths l_1 and l_2 and the Flory-Huggins interaction parameter χ_{12} for each temperature. Assess whether this χ_{12} compares with the one use measured earlier. Check whether this χ_{12} can be put into the familiar form $\chi_{12}=A+B/T$.

Factors Affecting the Scattered Intensity:

The scattered intensity $I(Q)$ is related to the absolute cross-section $d\Sigma(Q)/d\Omega$ by the expression:

$$I(Q) = \phi A d T (d\Sigma(Q)/d\Omega) \Delta\Omega \varepsilon t, \quad \text{Eq. 5}$$

where ϕ = flux on the sample,
 A = sample area,
 d = sample thickness,
 T = measured sample transmission,
 $\Delta\Omega$ = solid angle subtended by one pixel of the detector,
 ε = detector efficiency, and
 t = effective counting time, which was renormalized to give 10^8 monitor counts.

From this expression, one can observe that increasing either the sample area or sample thickness increases the intensity. The optimal sample thickness is

chosen for the condition $\Sigma_T d \sim 1$, i.e., $T = \exp[-\Sigma_T d] \sim 1/e = 37\%$ when scattering is dominated by incoherent scattering. Thickness corresponding to transmissions $T > 60\%$ are recommended for samples in which coherent scattering is strong. In practice, sample thickness is taken to be 1mm when the majority component is protonated (contains lots of hydrogen) and 2mm or even higher when the majority component is deuterated.

Complete Set of SANS Measurements

The counts on the detector result from several different sources:

- 1) scattering from the sample,
- 2) scattering from sources other than the sample and
- 3) stray neutrons and electronic noise.

These contributions are illustrated in Figure 5. Scattering from sources other than the sample can come from the sample holder, windows in the sample block or chamber, collimating slits and from air in the sample chamber. Sometimes it is also necessary to evacuate the sample chamber to greatly reduce air scattering in cases where it interferes with the signal from the sample itself. In order to subtract any remaining scattering from these other sources, an empty cell is measured under the same conditions as the sample. The empty cell is usually the sample holder, but it can simply be an empty beam, especially in cases where the sample is attached directly to a cadmium aperture. This type of background measurement is referred to as the “**empty beam**” measurement.

Contributions to the detector counts from stray neutrons, electronic noise, etc. are taken into account by making an additional measurement with the beam blocked by a neutron-absorbing material such as ^6Li . This background measurement is called the “**blocked beam**” measurement.

A good rule of thumb in deciding on the counting time for both types of background measurements is given by

$$\frac{t_{background}}{t_{sample}} = \sqrt{\frac{\text{Count Rate}_{background}}{\text{Count Rate}_{sample}}},$$

where t is the counting time. Thus, three measurements are needed in order to determine the scattering from the sample: **sample, empty beam and blocked beam**. These three **raw data measurements** are defined as follows:

$$I_{SAM} = C_O T_{sample+cell} \left(\left(\frac{d\Sigma(Q)}{d\Omega} \right)_{sample} + \left(\frac{d\Sigma(Q)}{d\Omega} \right)_{Empty\ Beam} \right) + I_{Blocked\ Beam},$$

$$I_{EMP} = C_O T_{cell} \left(\frac{d\Sigma(Q)}{d\Omega} \right)_{Empty\ Beam} + I_{Blocked\ Beam}, \text{ and}$$

$$I_{BGD} = I_{Blocked\ Beam},$$

where I is the measured intensity and T is the measured transmission. C_o is given by $C_o = \phi A d \Delta\Omega \varepsilon t$.

The raw SANS data are corrected for the empty beam and blocked beam contributions using

$$I_{COR} = (I_{SAM} - I_{BGD}) - \left(\frac{T_{sample+cell}}{T_{cell}} \right) (I_{EMP} - I_{BGD})$$

to obtain the scattering contribution arising only from the sample. This sample scattering is further corrected to account for any differences in detector sensitivity (~1%) from pixel to pixel. The detector sensitivity is measured by the instrument scientists each reactor cycle using an isotropic scattering material such as plexiglass or water. The correction is made by dividing the corrected sample scattering by the detector sensitivity, normalized to 1.0 count per pixel, on a pixel by pixel basis. This can be written as

$$I_{CAL} = \frac{I_{COR}}{\text{(Normalized Detector Sensitivity)}} = \phi A d T_{sample+cell} \left(\frac{d\Sigma(Q)}{d\Omega} \right)_{sample} \Delta\Omega \varepsilon t$$

In order to obtain the differential scattering cross-section of the sample, $\frac{d\Sigma(Q)}{d\Omega}$, in absolute units of cm^{-1} , the data must be put on an absolute scale by one of two methods: 1) the direct beam flux method or 2) the standard sample method. To use the direct beam flux method, measure a direct beam with nothing in the beam except an attenuator. Then, $I_{Direct} = \phi A T_{atten.} \Delta\Omega \varepsilon t$. The data are then put on an absolute scale using the relation

$$\left(\frac{d\Sigma(Q)}{d\Omega} \right)_{sample} = \left(\frac{I(Q)_{CAL}}{I_{Direct}} \right) \left(\frac{1}{d} \right) \left(\frac{T_{atten.}}{T_{sample+cell}} \right).$$

Alternatively, to use the standard sample method, a sample with known absolute scattering cross-section at $Q=0$, $\frac{d\Sigma(Q=0)}{d\Omega}$, must be measured in exactly the same instrument configuration as used for the experiment. Instrument scientists have previously determined $\frac{d\Sigma(Q=0)}{d\Omega}$ for several standard samples that are available for use. The measured intensity at $Q=0$ for the standard sample given by

$$I(Q=0)_{STD} = \phi A d_{STD} T_{STD+cell} \left(\frac{d\Sigma(Q=0)}{d\Omega} \right)_{STD} \Delta\Omega \varepsilon t.$$

The data are then put on an absolute scale using the relation

$$\left(\frac{d\Sigma(Q)}{d\Omega}\right)_{sample} = \left(\frac{I(Q)_{CAL}}{I(Q=0)_{STD}}\right) \left(\frac{d_{STD}}{d}\right) \left(\frac{T_{STD+cell}}{T_{sample+cell}}\right) \left(\frac{d\Sigma(Q=0)}{d\Omega}\right)_{STD}$$

These corrections are made within the user-friendly data reduction software package that uses IGOR.

Description of the NG3 30 m SANS Instrument:

The NG3 30 meter SANS instrument [4] is located in the guide hall of the NIST Center for Neutron Research (NCNR) facility, where it is installed at the end of a straight (6 x 6 cm²) neutron guide NG3. Designed to cover a wide Q range, from 0.015 to nearly 6 nm⁻¹, it is suitable for examining structural features in materials ranging from roughly 1 to 400 nm.

Before entering the neutron guide, neutrons from the 20 MW NCNR source are slowed down in the cold neutron moderator, or cold source (liquid hydrogen), which is cooled to approximately 20 K by cold helium refrigeration. An optical filter has been installed on the NG3 neutron guide in order to eliminate the gamma and epithermal neutron backgrounds by eliminating the direct line-of-sight to the cold source.

The layout of the instrument is shown in Figure 6. Neutrons from the cold source are monochromated mechanically by a helical channel velocity selector with variable speed and pitch which enables both the mean wavelength (0.5 to 2.0 nm) and wavelength spread (0.10 to 0.30 FWHM) to be varied.

The monochromated beam is collimated using circular pinhole irises in a 15 m long evacuated presample flight path. Incorporated into this flight path are eight 1.5 m long neutron guide sections that can be easily shifted in or out of the beam to vary the beam divergence and flux on sample by changing the effective source-to-sample distance from 3.5 m to 15 m in 1.5 m increments. The presample flight path boxes also contain beam-defining apertures and "empty" positions. The presample collimation is set by choosing the number of guides to be inserted in the beam. The guide motion software then inserts a "source" defining aperture just after the last guide and keeps all remaining downstream positions empty.

The instrument has two choices of sample location. (1) A permanently installed sample chamber (that can be used in air, under vacuum or under inert gas environment) with a computer-controlled sample stage. (2) A 60 cm diameter sample table, between the presample flight path and the sample chamber, which can accommodate large pieces of apparatus such as a Couette or Plate/Plate shear cell, a high-field electromagnet, a large cryostat, etc. Multi-specimen sample holders with temperature control (-10 to 200°C) are available for use in the sample chamber.

The post-sample flight path consists of a long cylindrical section that forms a vacuum enclosure for a large 2D position-sensitive neutron detector. The high count-rate area detector (64 cm x 64 cm with 0.5 cm spatial resolution) moves along rails that are parallel to the neutron beam (inside the cylindrical vessel). The sample-to-detector distance can be varied continuously from 1.3 m to 13.2 m. In addition, the detector moves transversely to the beam direction (by up to 30 cm) to extend the Q range covered at a given detector distance. The resulting Q range of the instrument extends approximately from 0.015 to 6 nm⁻¹.

The last presample flight path box of the NG3-SANS instrument contains two MgF₂ focussing devices: (1) a 30-lens system used with 8.4 Å neutrons and (2) a 7-lens/2-prism system that focusses 17.2 Å neutrons as well as corrects for gravity fall of the neutrons. These devices can be inserted into the beam and used with the following high-resolution instrument configuration: wavelength spread=14%, collimation=0 guide, neutron source diameter=1.43 cm, sample aperture diameter=1.59 cm, sample-to-detector distance=13.17 cm, beamstop size=2.54 cm. The 7-lens/2-prism system improves the minimum Q limit down to 0.0048 nm⁻¹ (=0.00048 Å⁻¹).

More extensive description of the NG3 SANS instrument can be found in the Data Acquisition manual (<http://www.ncnr.nist.gov/programs/sans/manuals/>).

SANS Instrument Configuration:

Estimate of the radius of gyration $R_g=100$ Å yields an estimate for $Q_{\min}<0.01$ Å⁻¹ (obtained from $Q_{\min}R_g<3^{1/2}$). The RPA model predictions for the hPEB/dPMB sample to be measured are given in Figure 4. Based on these predictions, the following instrument configuration is chosen using the SASCALC program.

***** SASCALC - NG3 *****

```
SOURCE APERTURE DIAMETER =                5.00 CM
SOURCE APERTURE TO SAMPLE APERTURE DISTANCE =    1002. CM
SAMPLE APERTURE TO DETECTOR DISTANCE =          910. CM
BEAM DIAMETER =                7.31 CM (UMBRA/PENUMBRA =.304)
BEAMSTOP DIAMETER =            7.62 CM
MINIMUM Q-VALUE =              0.0056 Å-1 (SIGMAQ/Q = 28.7 PERCENT)
MAXIMUM HORIZONTAL Q-VALUE =          0.0604 Å-1
MAXIMUM VERTICAL Q-VALUE =          0.0372 Å-1
MAXIMUM Q-VALUE =              0.0709 Å-1 (SIGMAQ/Q = 6.5 PERCENT)
BEAM INTENSITY =                1727752. COUNTS / SEC.
( FIGURE OF MERIT =              0.622E+08 Å2 / S )
ATTENUATOR TRANSMISSION =          0.30E-02 (POS#7) (FOR
TRANSMISSION RUNS)
```

- 1) SAMPLE APERTURE DIAMETER = 1.27 CM
- 2) NUMBER OF GUIDES = 4
- 3) SAMPLE CHAMBER TO DETECTOR DISTANCE = 900. CM
- 4) TABLE POSITION: (1= HUBER, 2=CHAMBER) 2
- 5) DETECTOR CENTER OFFSET 20.00 CM
- 6) NEUTRON WAVELENGTH 6.00 Å

- 7) WAVELENGTH SPREAD, FWHM 0.150
8) SAMPLE APERTURE TO SAMPLE POSITION DISTANCE 10.00 CM

References:

1. P.G. de Gennes, "Scaling Concepts in Polymer Physics", (Cornell U., 1979)
2. B. Hammouda, N.P. Balsara and A.A. Lefebvre, "SANS from Pressurized PEB/PMB", *Macromolecules* 18, 5572 (1997)
3. N.P. Balsara, A.A. Lefebvre, J.H. Lee, C.C. Lin and B. Hammouda, "Search for a Model Polymer Blend", *AIChE Journal*, 44, 2515 (1998)
4. C. Glinka, J. Barker, B. Hammouda, S. Krueger, J. Moyer and W. Orts, "The 30 m SANS Instruments at NIST", *J. Appl. Cryst.* 31, 430 (1998)

The following SANS manuals and relevant tutorials can be found on the Web at <http://www.ncnr.nist.gov/programs/sans/>

- >> SANS data reduction manual
- >> IGOR SANS data reduction manual
- >> A Tutorial on SANS from Polymers
- >> Description of the 30m SANS Instrument
- >> Fundamental of SANS
- >> SANS Experimental Methods

Polymer Blends

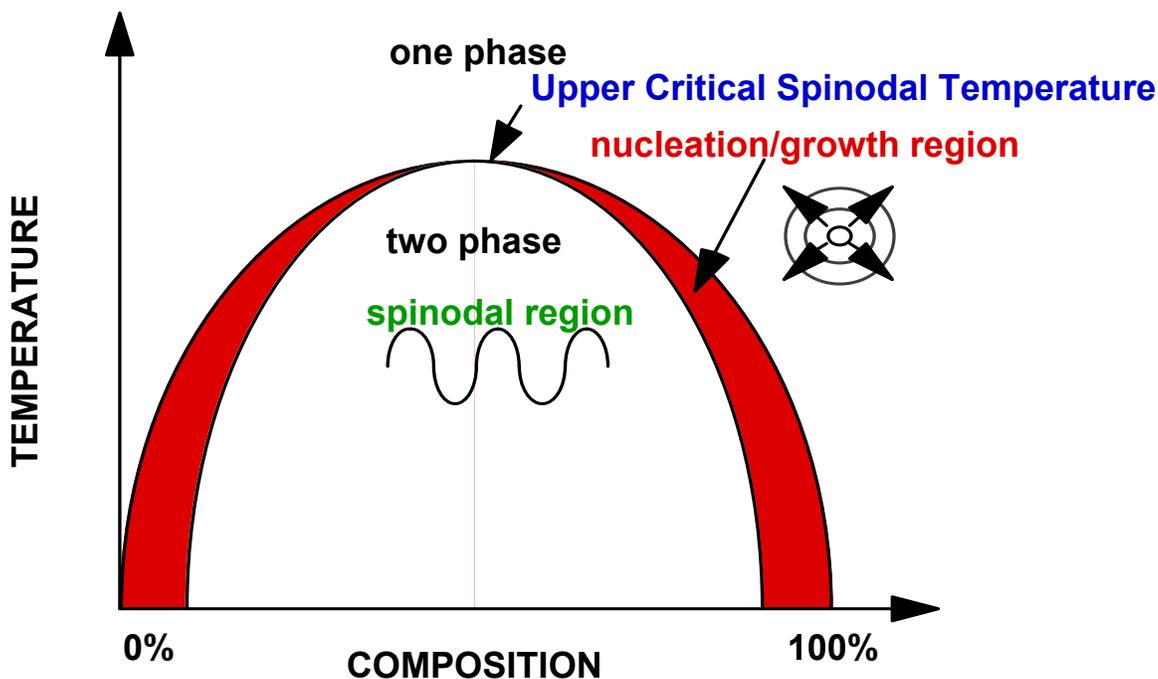


Figure 1: Phase separation diagram for polymer blend mixtures.

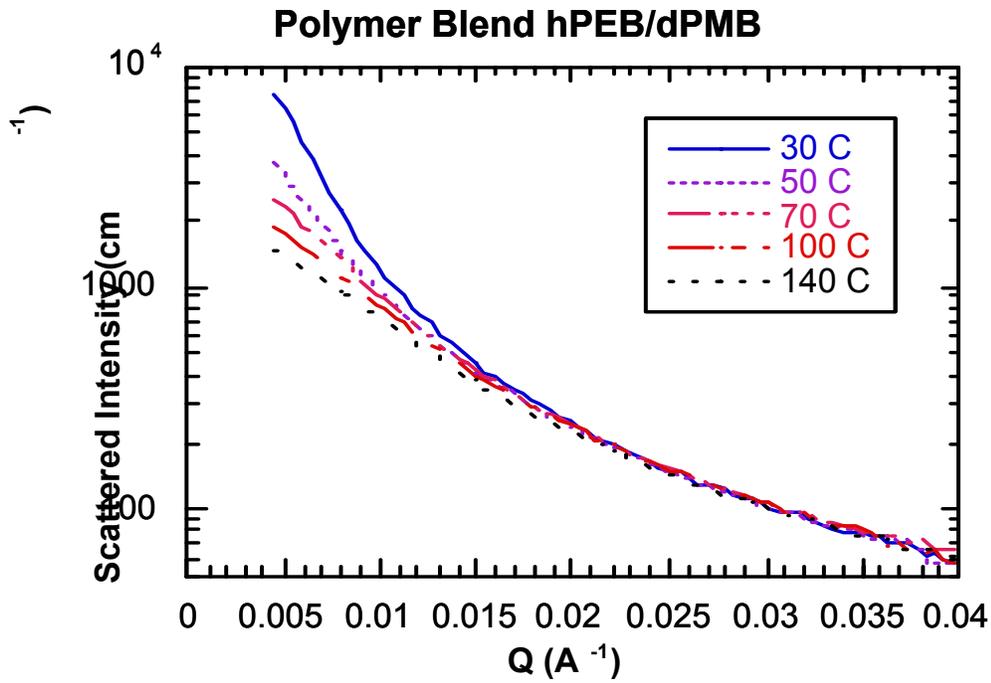


Figure 2: Averaged SANS data from a polyolefin polymer blend (hPEB/dPMB with $M_w=200K/200K$ and composition of 25%/75%). The sample is different from the sample to be measure.

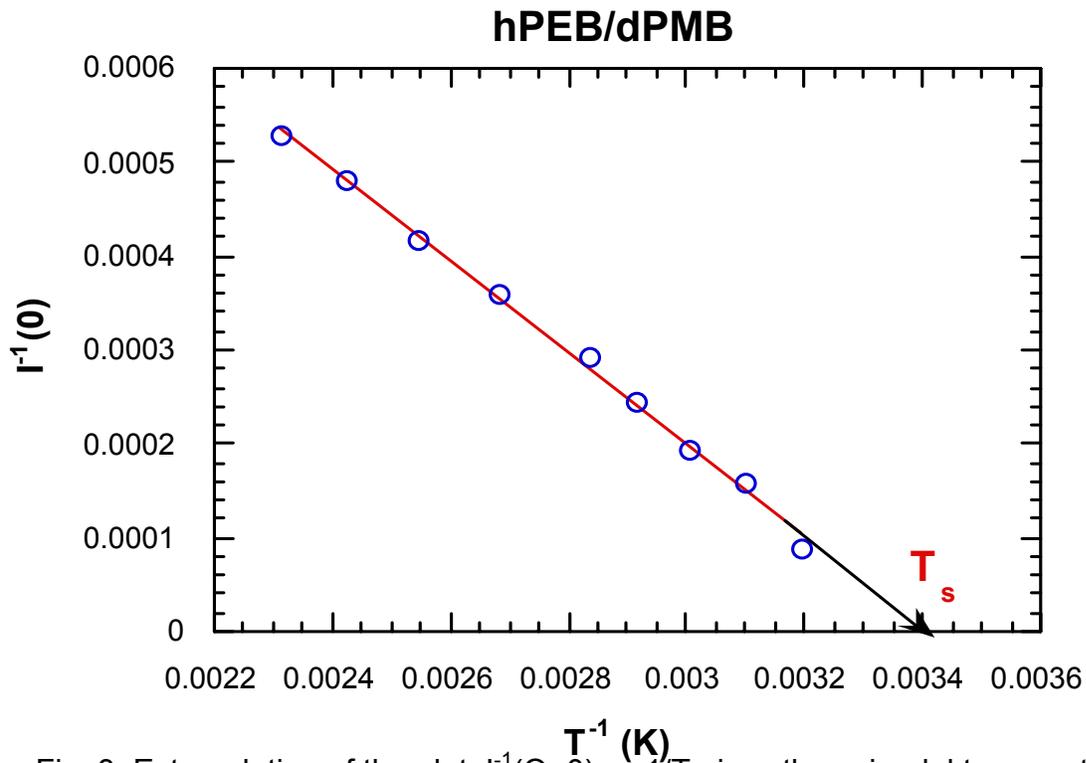


Fig. 3. Extrapolation of the plot, $I^{-1}(Q=0)$ vs $1/T$ gives the spinodal temperature.

inputnames	inputvalues
Deg. Polym. Nc	525
Vol. Frac. Phic	0.57
Spec. Vol. Vc	97.5
Scatt. Length Lc	-5e-13
Deg. Polym. Nd	1105
Vol. Frac. Phid	0.43
Spec. Vol. Vd	81.9
Scatt. LengthLd	5.33e-12

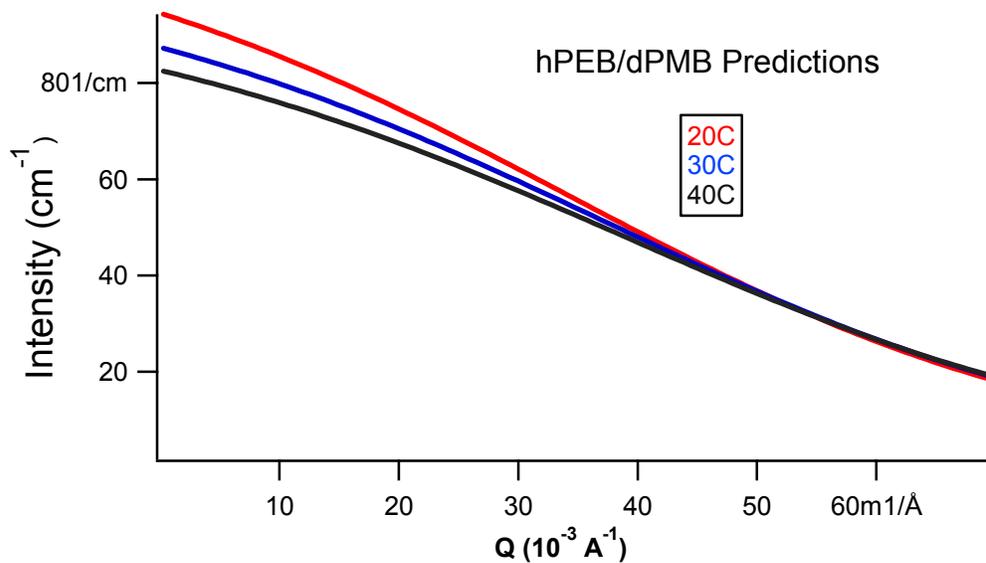


Figure 4: Predicted SANS intensity from the hPEB/dPMB sample to be measured based on the Random Phase Approximation mode.

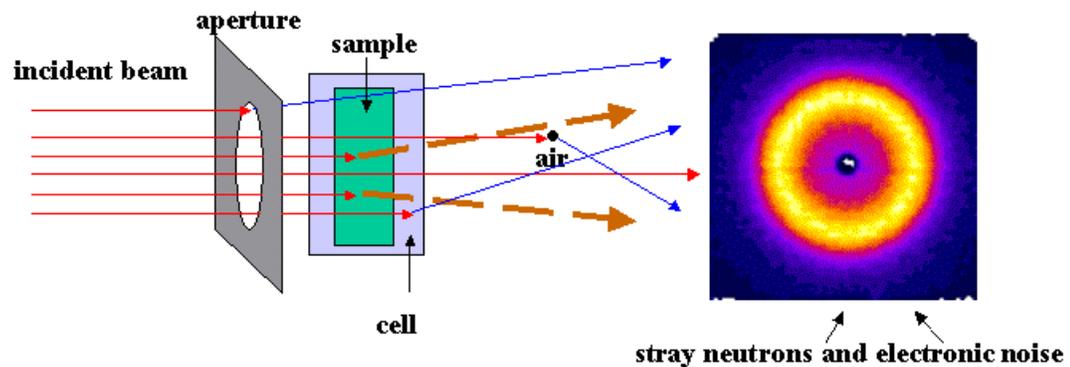
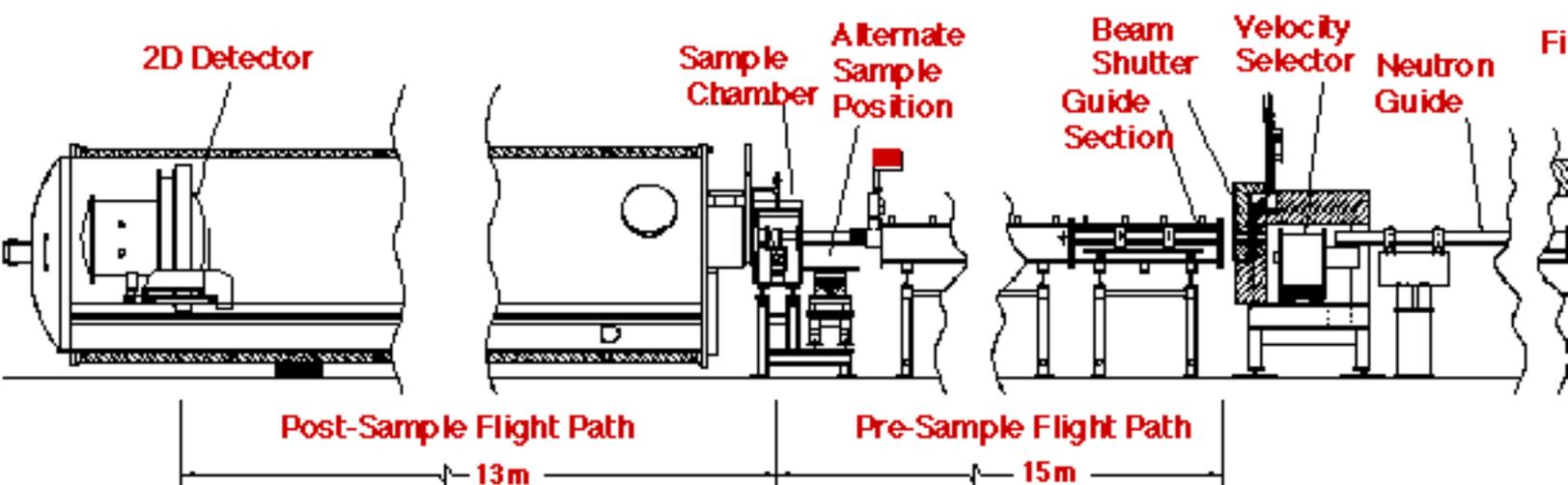


Figure 5: Various contributions to scattering.

CHRNS 30 METER SANS INSTRUMENT



λ : 0.5 to 2.0 nm, $\Delta\lambda/\lambda$: 10 to 30 %
 Q : 0.015 to 6 nm⁻¹, feature size: 1 to 400 nm
 pinhole collimation. $Q_{\min} = 0.0048 \text{ nm}^{-1}$

Pre/Post sample paths variable,
 high count-rate detector,
 all aspects of the instrument
 are computer-controlled.

NIST
 National Institute of Standards and Technology



Figure 6: Schematic of the NG3 SANS instrument.